Ludwig Boltzmann and Entropy

The second law of thermodynamics is probably the single most important macroscopic law of physics. It originates in the idea that heat flows from hot bodies to cold bodies. It tells us that in converting heat to work we can't break even, that some heat has to be wasted. It tells us that things run down, that the *entropy* of an isolated system can never decrease. But what is entropy? Thermodynamics shows that there is such a quantity, that it is a function of the *state* of the system, not of its history, and that for an infinitesimal quasistatic process at temperature T, if a quantity q of heat is absorbed then the change in the entropy is q/T. It even tells us how to *measure* the entropy. But despite these great successes, thermodynamics is a *macroscopic* theory, so it doesn't and can't relate entropy to quantities arising in a microscopic, dynamical description of the system. Boltzmann's extraordinary intellectual leap lay in uncovering the *microscopic* meaning of entropy, in answering the question, "what is entropy?"

So what did Boltzmann do?

- He *defined* entropy as log Ω where Ω is the number of microstates accessible to the system. From this definition flows all of thermodynamics and statistical physics.

- He explained in statistical terms the second law of thermodynamics, i.e., that entropy must in general increase for an isolated system, and showed how such "irreversible" behaviour could follow from the time-symmetric laws of mechanics.

- He constructed an approximate but very useful model (the Boltzmann transport equation) to describe how the distribution of positions and velocities of the particles of a gas evolves in time under flow and collisions.

- His work, in particular the idea of counting microstates, relied in a fundamental way on the idea that matter was composed of discrete atoms. Its success, and his impassioned defence of these ideas, established atomism once and for all.

Below, I summarise briefly the course of Boltzmann's life and work. More on the subject can be found in the various 'entropy articles' in this special issue dedicated to him, as well as in others to which I refer at the end.

Ludwig Eduard Boltzmann was born in Vienna on 20 February 1844. His father was a government official, which meant that the family could afford to let young Ludwig pursue higher studies rather than earn a living. He took his doctorate in physics in 1866, working on the kinetic theory of gases. His PhD advisor was Josef Stefan, whose name most high-school and college students remember in connection with the Stefan-Boltzmann law for the flux of radiation from a hot body. Recall that in the late 19th century atoms were not a firmly established reality, despite the successes of the kinetic theory of gases. There were 'energists', such as Ernst Mach and Wilhelm Ostwald, who held that there was no need to explain, or to reduce to any other form, the kind of energy known as heat. In particular, they were oppposed to any talk of atoms since no one had actually seen any – an extreme positivist position. Boltzmann, a staunch 'atomist', saw that the only way to explain or derive thermodynamics from mechanics was to think of a gas as made of discrete atoms, and to count the number of ways their positions and velocities could be distributed. Atomism was thus vital to Boltz-mann, since without it his *statistical mechanics* could not exist. The energists were content to live with thermodynamics as an independent set of laws, at least until such time as someone gave them direct evidence, whatever that might mean, for atoms.

Boltzmann took his disputes with the energists very much to heart; after one such argument, with Ostwald, he was so upset that he attempted suicide. In general, these disagreements led to his moving around a great deal during his academic career. Until 1869 he remained in Vienna as a lecturer, then moved to a chair in Theoretical Physics at the University of Graz. He returned to Vienna as Professor of Mathematics in 1873, went back to Graz as Professor of Experimental Physics in 1876, where he married Henriette von Aigentler, whom he had met during his earlier stay there. He stayed at Graz until 1890, when he moved to the University of Munich as Professor of Theoretical Physics. He *returned*, however, to Vienna as Professor of Theoretical Physics in 1894, only to move once again, this time to Leipzig, in 1900. He left Leipzig for Vienna again, in 1902, where his position had been held for him.

Let us now understand, very briefly, Boltzmann's notion of entropy. Consider a macroscopic system, say a box of gas, in a state characterised by a set of (macroscopic) variables M, such as volume, temperature, and number of particles. Clearly, one can change the *microscopic* state of the system (the set of positions and momenta of all the particles) in many different ways without changing the macrostate M. Indeed, such changes of microstate happen constantly in a gas: molecules move around at high speed, scatter off each other, and bounce off the walls, with no perceptible change in the macroscopically measured properties. Let W be the number of microstates corresponding to the macrostate M. Then, said Boltzmann, the entropy

$$S = k \log W , \qquad (1)$$

where the constant k is Boltzmann's constant relating energy and temperature, which the reader will have encountered while studying the kinetic theory of gases. The version (1), which appears on Boltzmann's tombstone, is actually Max Planck's rendition of Boltzmann's broader statement $S \propto \log W$. How do you determine W? The microstate, as defined above, of a gas of N particles in 3 dimensions is clearly a point in a space of dimension $6N$ (3 position coordinates and 3 momenta per particle), called the *phase space* of the system. This space is a continuum, so what we mean by the 'number of states' is simply the volume (generalised to $6N$ dimensions) of phase space occupied by the gas molecules.

The definition (1) is more natural, in retrospect, than you might first think. For the ideal gas (see Jayanta Bhattacharjee's article in this issue) one can carry out explicitly both the state-counting argument and the thermodynamic calculation and see that they agree. Thus it becomes clear that entropy is intimately associated with the number of microstates for a given macrostate. Secondly, instead of (1), let us make the weaker assumption $S = f(W)$, without specifying the functional form of f. Now consider two systems, labelled 1 and 2, which do not interact with each other. If the systems have W_1 and W_2 states respectively then the total number of states of the combined system is $W = W_1 W_2$. Thus the total entropy $S = f(W) = f(W_1 W_2)$. But since the systems are noninteracting, $S = S_1 + S_2$ since thermodynamics tells you entropies are additive. This implies $f(W) \propto \log W$, which is Boltzmann's result. Incidentally, the energists or positivists didn't like W either; they said it couldn't be measured directly.

Boltzmann then explained why the Second Law of Thermodynamics had to hold. We can see this from an example: imagine N particles allowed to occupy a volume V and, for convenience, let us specify positions to an accuracy v in volume. Initially, let us constrain the particles to sample only a volume $V/2$, i.e, half the box. Then each particle can be placed in any one of $V/2v$ locations, so that the total number of ways you could put down N particles (i.e., the total number of microstates) would be $W = (V/2v)^N$. The entropy, from equation (1), is $S(V/2) = k \log W = N k \log (V/2v)$. Now remove the constraint and allow access to the whole volume V. The number of microstates is now $(V/v)^N$, which is larger by a factor of 2^N than that for the constrained case (and remember that $N \sim 10^{23}$). Thus, if the system is started out in a typical state corresponding to a volume $V/2$, and allowed to evolve with constraints removed, it will *typically* find itself (unless the dynamics was peculiar to the point of perversity), in one of the microstates corresponding to the full volume V, since these are overwhelmingly larger in number. The entropy will then increase from the value $S(V/2)$ to the value $S(V) = N k \log (V/v) = S(V/2) + N k \log 2$ as the particles explore the box. In effect, the words 'typical' and 'typically' in the above argument attracted the criticism of Zermelo and Loschmidt. They argued that the time-reversible nature of classical mechanics could not possibly result in this sort of irreversible behaviour, that given enough time the gas mentioned in the example above would return to a state in which it occupied only half the box. Boltzmann's response was that such 'returns' could certainly occur, but that they were overwhelmingly unlikely (by a factor exponential in N), and that he was talking of the expected behaviour in the mean. In other words, he said, the Second Law is a *statistical* law.

Boltzmann took his own life in 1906 while on holiday with his wife and daughter at Duino (near Trieste, now in Italy). It is said that he was driven to suicide partly because of a fear that his ideas were not accepted by the community, that the battle against energism was lost. It is clear, though, that his genius was recognised even by those who disagreed with him: he couldn't otherwise have quit so many positions and still have managed to get new ones at will. I wonder whether our system would have dealt so kindly with him.

When you're done with this issue, you can read more about entropy, Boltzmann and irreversibility in the following articles available at the Los Alamos archive:

S Goldstein (http://arXiv.org/abs/cond-mat/0105242)
D Flamm (http://arXiv.org/abs/physics/9710007)
J Lebowitz (http://arXiv.org/abs/math-phys/0010018).

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